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MATRIC NUMBER: 19/MHS02/021

COURSE: CHEMISTRY 102

DEPARTMENT: NUSRING

ASSIGNMENT ON CARBOXYLIC ACID

Q1. Give the IUPAC names of the following compounds. (i) HCOOH (ii) $HOOCCH_2CH_2CH_2COOH$ (iii) $CH_3CH_2CH_2COOH$ (iv) $HO_2C\text{-}CO_2H$ (v) $CH_3(CH_2)_4COOH$ (vi) $CH_3CH{=}CHCH_2CH_2COOH$.

Q2. Discuss briefly the physical properties of carboxylic acids under the following headings; (i) Physical appearance (ii) Boiling point (iii) Solubility.

Q3. Write two industrial preparations of carboxylic acids.

Q4. With equations and brief explanation, discuss the synthetic preparation of carboxylic acid.

Q5. With chemical equation only, outline the reduction, decarboxylation and esterification of carboxylic acid.

SOLUTIONS

Q1. (i) Methanoic acid (ii) Pentan-1,5-dioic acid (iii) Butanoic acid (iv) Ethanedioic acid (v) Hexanoic acid (vi) Hex-4-eneoic acid.

Q2. Physical properties of carboxylic acid:

- Physical appearance: All simple aliphatic carboxylic acids up to C_{10} are liquids at room temperature. Most other carboxylic acids are solid at room temperature although anhydrous carboxylic acid (acetic acid) also known as glacial ethanoic acid freezes to an ice like solid below the room temperature.
- Boiling point: Boiling point increases with increasing relative molecular mass. Aromatic carboxylic acids are crystalline solids and have higher melting points than their aliphatic counterparts of comparable relative molecular mass.
- Solubility: Lower molecular mass carboxylic acids with up to four carbon atoms in their molecules are soluble in water; this is due to their ability

to form hydrogen bonds with their water molecules. The water solubility of the acids decreases as the relative molecular mass increases because the structure becomes relatively more hydrocarbon in nature and hence covalent. All carboxylic acids are soluble in organic solvents.

Q3. Industrial preparation of carboxylic acid:

- From Carbon (II) oxide: Methanoic acid (formic acid) is manufactured by adding carbon (II) oxide under pressure to hot aqueous solution of sodium hydroxide. The free carboxylic acid is liberated by careful reaction with tetraoxosulphate (vi) acid (H_2SO_4)

$$CO \xrightarrow{NaOH} HCOONa \xrightarrow{H_2SO_4} HCOOH + NaHSO_4$$

- From petroleum: Liquid phase air oxidation of C_5-C_7 alkanes, obtainable from petroleum at high temperature and pressure will give C_5-C_7 carboxylic acids with methanoic, propanoic and butanedioic acids as by-products.

$$C_5\text{-}C_7 \xrightarrow{O_2/\text{High temperature and pressure}} C_5\text{-}C_7 \text{ carboxylic acids}$$

Q4. Synthetic preparation of carboxylic acid

- Oxidation of primary alcohols and aldehydes: Oxidation of primary alcohols and aldehydes can be used to prepare carboxylic acids using the usual oxidizing agents (i.e $K_2Cr_2O_7$ or $KMnO_4$) in acidic solution

$$RCH_2OH \xrightarrow{[O],\ \text{excess acid}/KMnO_4} RCHO \xrightarrow{[O]} RCOOH$$

- Carbonation of Grignard reagent: Aliphatic carboxylic acids are obtained by bubbling carbon (IV) oxide into the Grignard reagent and then hydrolyzed with dilute acid

$$RMgBr + CO_2 \xrightarrow{(C_2H_3)_2O} RCOOMgBr \xrightarrow{H_2O/\text{dil. acid}} RCOOH + MgBrOH$$

R may be 1^0, 2^0, 3^0 aliphatic alkyl or aryl radical

In the preparation of benzoic acid, the reagent is added to solid carbon (IV) oxide (dry ice) which also serves as coolant to the reaction mixture

$$C_6H_5MgBr + CO_2 \xrightarrow{(C_2H_5)_2O} C_6H_5COOMgBr \xrightarrow{H_2O/H^+} C_6H_5COOH + MgBrOH$$

- Hydrolysis of nitriles (cyanides) or esters

$$RCN + 2H_2O \xrightarrow{H^+} RCOOH + NH_4^+$$

(R= alkyl or aryl radical)

$$RCOOR' \xrightarrow{H_2O/H^+ \text{ reflux}} RCOOH + R'OH$$

$$C_6H_5CH_2CN + 2H_2O \xrightarrow{H^+} C_6H_5CH_2COOH + NH_4^+$$

$$CH_3CH_2COOCH_3 \xrightarrow{H_2O/H^+ \text{ reflux}} CH_3CH_2COOH + CH_3OH$$

Q5. Reduction:

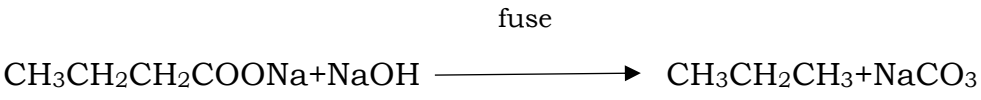
$$4RCOOH + 3LiAlH_4 \xrightarrow{(C_2H_5)_2} (RCH_2O)_4\,AlLi + 2LiAlO_2 + 4H_2$$

$$(RCH_2O)_4\,AlLi \xrightarrow{4H_2O} 4RCH_2OH + Al(OH)_3 + LiOH$$

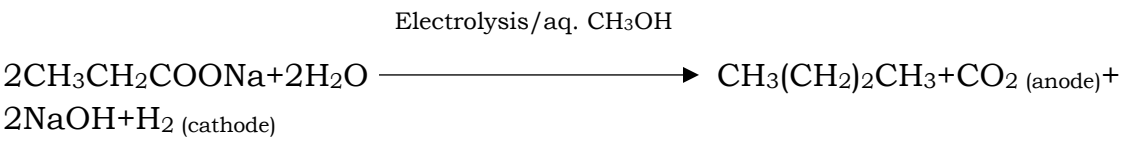
$$CH_3CH_2CH_2COOH \longrightarrow CH_3CH_2CH_2CH_2OH$$

Butanoic acid — Butanol

Decarboxylation:



Kolbe synthesis



Esterification: